

Transition properties from the Hermitian formulation of the coupled cluster polarization propagator

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Theory of one-electron transition density matrices has been formulated within the time-independent coupled cluster method for the polarization propagator [R. Moszynski, P. S. Żuchowski, and B. Jeziorski, *Coll. Czech. Chem. Commun.* **70**, 1109 (2005)]. Working expressions have been obtained and implemented with the coupled cluster method limited to single, double, and linear triple excitations (CC3). Selected dipole and quadrupole transition probabilities of the alkali earth atoms, computed with the new transition density matrices are compared to the experimental data. Good agreement between theory and experiment is found. The results obtained with the new approach are of the same quality as the results obtained with the linear response coupled cluster theory (LRCC). The one-electron density matrices for the ground state in the CC3 approximation have also been implemented. The dipole moments for a few representative diatomic molecules have been computed with several variants of the new approach, and the results are discussed to choose the approximation with the best balance between the accuracy and computational efficiency.

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I. INTRODUCTION

One of the most challenging problems of modern quantum chemistry is an accurate and fast computation of molecular properties. Coupled cluster theory (CC) which is the gold standard of quantum chemical methods, combines an accurate description of the electronic structure with an affordable computational cost for medium sized molecules. The coupled cluster Ansatz is presented as¹⁻⁹

$$\Psi = e^T \Phi, \tag{1}$$

where the cluster operator T for an N electron system is the sum of single, double, and higher excitations, $T = T_1 + T_2 + \dots + T_N$, and Φ is the reference function. Due to the exponential form of the Ansatz, the CC theory is size-extensive for any truncation of T . The possibility of restricting T to a particular excitation level introduces a hierarchy of approximations: coupled cluster singles and doubles (CCSD), coupled cluster singles, doubles, and triples (CCSDT), etc. Also, the methods CC2¹⁰ and CC3,¹¹ approximating CCSD and CCSDT, respectively, were developed. The CC3 equations for T_1 and T_2 have the same form as in CCSDT. The equation for T_3 , however, includes only terms up to the second order in the fluctuation potential. The CC3 approximation ensures that the triple amplitudes are correct through the second order, while there is no need for storing T_3 in memory: they are readily computable on the fly with expressions including single and double excitations. The ground state CC3 model scales as \mathcal{N}^7 , whereas CCSDT scales as \mathcal{N}^8 , with the size of the basis \mathcal{N} .

Currently, molecular properties of the ground state within the CC framework are computed as the derivative of the first-order Lagrangian with respect to the field strength.^{12,13} An alternative method, referred to as XCC, was proposed by Jeziorski and Moszynski¹⁴ and further investigated by Moszynski et al.^{15,16}, Korona and Jeziorski¹⁷ and Korona, Przybytek, and Jeziorski¹⁸. In the XCC approach, the first-order properties are computed directly from the definition of the quantum-mechanical expectation value. This formalism is conceptually simple and its computational cost is lower than in the case of the Lagrangian technique as it does not require finding the expensive left-hand solution of the CC equations, the so-called Λ or Z vector.^{12,13}

The main object of interest in this study is the linear response function $\langle\langle X; Y \rangle\rangle_\omega$, often referred to in the literature as the polarization propagator. The linear response function describes the response of an observable X to the perturbation Y oscillating with the fre-

quency ω . The residues of the polarization propagator are connected to many physical observables, e.g. transition probabilities, lifetimes, and line strengths. For real ω and for purely real or purely imaginary perturbations Y , the polarization propagator satisfies the following relation

$$\langle\langle X; Y \rangle\rangle_{\omega} = \langle\langle X; Y \rangle\rangle_{-\omega}, \quad (2)$$

which reflects the time-reversal symmetry.

The linear response function within CC theory can be computed either from the response theory (LRCC),^{19–21} or from the time-independent XCC theory.²² Both theories give the polarization propagator satisfying Eq. (2). In the LRCC approach the time-reversal symmetry of the linear response function follows from the restriction of the time-dependent expectation value to the real part, which is otherwise not guaranteed to be real if an approximate coupled cluster wave function is employed. In XCC, one starts from the exact expression for the polarization propagator. Thus, the correct symmetry is present in the XCC theory from the start. The final form of the polarization propagator in this theory is Hermitian in the sense that any truncation of the cluster operators does not violate the correct time-reversal symmetry.

During the twenty years since the initial formulation of the XCC method,¹⁴ numerous studies restricted to the CCSD level were reported: electrostatic¹⁵ and exchange¹⁶ contributions to the interaction energies of closed-shell systems, first-order molecular properties,¹⁷ static and dynamic dipole polarizabilities,¹⁸ frequency-dependent density susceptibilities employed in SAPT(CC).²³ In this paper we present the derivation and implementation of the transition density matrices obtained from the XCC linear response function²² at the CC3 level. Also, the results for the first-order one-electron properties at the CC3 level are presented in order to test various approximations to the XCC theory.

This paper is organized as follows. In section II we derive the formula for the first-order properties within the XCC3 theory. We also report the derivation of the transition density matrices from the XCC linear response function. Next, in section III we present the numerical results for the ground-state dipole moments of some representative diatomic molecules. We discuss various approximations to the XCC3 theory that offer the best balance between the accuracy and computational efficiency. We continue the discussion of the results with the atomic dipole and quadrupole transition probabilities computed within the XCC3

theory. Whenever possible, extensive comparison with the experimental data as well as with the data obtained from the LRCC3 calculations is reported. Finally in section IV we conclude our paper.

II. THEORY

A. Basic definitions

All the operators in this work are expressed through the singlet orbital replacement operators²⁴

$$E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad (3)$$

which satisfy the commutation relation $[E_{pq}, E_{rs}] = E_{ps}\delta_{rq} - E_{rq}\delta_{ps}$. From now on, $a, b, c \dots$ and $i, j, k \dots$ denote virtual and occupied orbital indices, respectively, and $p, q, r \dots$ general indices. The cluster operator T is represented in a compact form as a sum of n -tuple excitation operators T_n ,

$$T_n = \frac{1}{n!} \sum_{\mu_n} t_{\mu_n} \mu_n, \quad (4)$$

where μ_n stands for the product of the n singlet excitation operators $E_{ai}E_{bj} \dots E_{fm}$. The CC amplitudes satisfy the following permutation symmetry relations

$$\begin{aligned} t_{ij}^{ab} &= t_{ji}^{ba} \\ t_{ijk}^{abc} &= t_{ikj}^{acb} = t_{jik}^{bac} = t_{jki}^{bca} = t_{kij}^{cab} = t_{kji}^{cba}. \end{aligned} \quad (5)$$

The excitation energies in this work are obtained from the diagonalization of the CC Jacobian matrix,^{19,25,26}

$$A_{\mu_n \mu_m} = \langle \tilde{\mu}_n | [e^{-T} H e^T, \mu_m] \rangle, \quad (6)$$

where we introduce the shorthand notation $\langle X|Y \rangle = \langle X\Phi|Y\Phi \rangle$, $\langle X \rangle = \langle \Phi|X\Phi \rangle$. The elements of the Jacobian are defined in the biorthonormal basis

$$\langle \tilde{\mu}_n | \nu_n \rangle = \delta_{\mu_n \nu_n} \quad (7)$$

For the single and double excitation manifold we used the basis proposed by Helgaker, Jorgensen, and Olsen²⁶. A biorthonormal and nonredundant basis for the triply excited

manifold is derived in the Appendix.

The expectation value of an observable in the XCC theory is given by the explicitly connected, size-consistent expression introduced by Jeziorski and Moszynski¹⁴

$$\bar{X} = \langle e^{S^\dagger} e^{-T} X e^T e^{-S^\dagger} \rangle. \quad (8)$$

The auxiliary operator $S = S_1 + S_2 + \dots + S_N$ is the solution of the following equation

$$\begin{aligned} S_n = T_n - \frac{1}{n} \hat{\mathcal{P}}_n \left(\sum_{k=1} \frac{1}{k!} [\tilde{T}^\dagger, T]_k \right) \\ - \frac{1}{n} \hat{\mathcal{P}}_n \left(\sum_{k=1} \sum_{m=0} \frac{1}{k!} \frac{1}{m!} [[\tilde{S}, T^\dagger]_k, T]_m \right), \end{aligned} \quad (9)$$

where

$$\tilde{T} = \sum_{n=1}^N n T_n, \quad \tilde{S} = \sum_{n=1}^N n S_n, \quad (10)$$

and

$$[A, B]_k = \underbrace{[[\dots [A, B], B] \dots]}_{\text{nested } k \text{ times}}. \quad (11)$$

The superoperator $\hat{\mathcal{P}}_n(X)$ projects the n -tuple excitation part of an arbitrary operator X

$$\hat{\mathcal{P}}_n(X) = \frac{1}{n!} \sum_{\mu_n} \langle \tilde{\mu}_n | X \rangle \mu_n. \quad (12)$$

The expanded expression for S_n , Eq. (9), is finite, though it contains cumbersome terms with multiply-nested commutators. These terms are of high order in the fluctuation potential.¹⁴ Also, the r.h.s. of Eq. (9) depends on S , therefore solving this equation requires an iterative procedure. However, S can efficiently be approximated while retaining the size consistency of the expectation value expression. Below, we present the expressions for $S_n(m)$ for $n \in \{1, 2, 3\}$ and $m \in \{2, 3, 4\}$, with m denoting the highest many-body perturbation theory (MBPT) order fully included,

$$\begin{aligned}
S_1(2) &= T_1 \\
S_1(3) &= S_1(2) + \hat{\mathcal{P}}_1 \left([T_1^\dagger, T_2] \right) \\
&\quad + \hat{\mathcal{P}}_1 \left([T_2^\dagger, T_3] \right) \\
S_1(4) &= S_1(3) + \hat{\mathcal{P}}_1 \left([[T_2^\dagger, T_1], T_2] \right) \\
&\quad + \frac{1}{2} \hat{\mathcal{P}}_1 \left([[T_3^\dagger, T_2], T_2] \right) \\
S_2(2) &= T_2 \\
S_2(3) &= S_2(2) + \frac{1}{2} \hat{\mathcal{P}}_2 \left([[T_2^\dagger, T_2], T_2] \right) \\
S_2(4) &= S_2(3) + \hat{\mathcal{P}}_2 \left([T_1^\dagger, T_3] \right) \\
S_3(2) &= T_3 \\
S_3(4) &= S_3(3) + \frac{1}{2} \hat{\mathcal{P}}_3 \left([[T_1^\dagger, T_2], T_2] \right) \\
&\quad + \hat{\mathcal{P}}_3 \left([[T_2^\dagger, T_2], T_3] \right)
\end{aligned} \tag{13}$$

We test the accuracy of three approximations denoted as XCC3S(m), with $m = 2, 3, 4$

$$\begin{aligned}
\text{XCC3S}(2) &: S_1(2) + S_2(2) + S_3(2) \\
\text{XCC3S}(3) &: S_1(3) + S_2(3) + S_3(2) \\
\text{XCC3S}(4) &: S_1(4) + S_2(4) + S_3(2).
\end{aligned} \tag{14}$$

One should note that in all three approximations $S_3 = T_3$.

The accuracy of S depends on the underlying wave function model. The CC3 method includes T_1 and T_2 correct through the third order and T_3 correct through the second order. The accuracy of S_1 , S_2 , and S_3 is of the same order of MBPT as the accuracy of the corresponding T_1 , T_2 , and T_3 amplitudes. The lowest order contributions to S_4 are of the third order, but this quantity appears only in the fourth order contributions to the transition density matrices, and is not required.

Using the commutator expansion in Eq. (8) we obtain the following formula for the

expectation value of an operator at the CC3 level of theory

$$\begin{aligned}
\bar{X} &= \sum_{\mathcal{M}=0}^8 \bar{X}^{(\mathcal{M})} = \langle X \rangle^{(0)} \\
&+ \langle S_1 | X \rangle^{(2)} + \langle [X, T_1] \rangle^{(2)} + \langle S_2 | [X, T_2] \rangle^{(2)} \\
&+ \langle S_1 | [X, T_2] \rangle^{(3)} + \langle S_2 | [X, T_3] \rangle^{(3)} \\
&+ \langle S_1 | [X, T_1] \rangle^{(4)} + \langle S_2 | [[X, T_1], T_2] \rangle^{(4)} \\
&+ \langle S_3 | [X, T_3] \rangle^{(4)} + \frac{1}{2} \langle S_3 | [[X, T_2], T_2] \rangle^{(4)} \\
&+ \frac{1}{2} \langle S_1^2 | [X, T_2] \rangle^{(5)} + \frac{1}{2} \langle S_1 S_2 | [[X, T_2], T_2] \rangle^{(5)} \\
&+ \frac{1}{2} \langle S_1 S_2 | [X, T_3] \rangle^{(5)} \\
&+ \frac{1}{2} \langle S_1 | [[X, T_1], T_1] \rangle^{(6)} + \frac{1}{2} \langle S_1^2 | [X, T_3] \rangle^{(6)} \\
&+ \frac{1}{2} \langle S_1^2 | [[X, T_1], T_2] \rangle^{(7)} \\
&+ \frac{1}{12} \langle S_1^3 | [[X, T_2], T_2] \rangle^{(8)} + \frac{1}{6} \langle S_1^3 | [X, T_3] \rangle^{(8)}.
\end{aligned} \tag{15}$$

The upper index of $\bar{X}^{(\mathcal{M})}$ indicates an \mathcal{M} -th order contribution. Apart from T_n and S_n for $n > 3$, no other approximations have been introduced in Eq. (15).

B. XCC3 transition density matrices

In the exact theory the polarization propagator is defined by the following expression²⁷

$$\begin{aligned}
\langle \langle X; Y \rangle \rangle_\omega &= - \left\langle \Psi_0 \left| Y \frac{Q}{H - E_0 + \omega} X \Psi_0 \right. \right\rangle \\
&- \left\langle \Psi_0 \left| X \frac{Q}{H - E_0 - \omega} Y \Psi_0 \right. \right\rangle,
\end{aligned} \tag{16}$$

where H denotes the Hamiltonian, Ψ_0 is the normalized ground-state wave function, E_0 is the ground state energy, and Q is the projection operator on the space spanned by all excited states. The line strength S_{XY}^{0K} of the transition to the K -th excited state is obtained

as the residue of the linear response function:

$$\lim_{\omega \rightarrow \omega_K} (\omega - \omega_K) \langle \langle X; Y \rangle \rangle_\omega = \sum_{K'} \langle \Psi_0 | X \Psi_{K'} \rangle \langle \Psi_{K'} | Y \Psi_0 \rangle = S_{XY}^{0K} \quad (17)$$

$$\lim_{\omega \rightarrow -\omega_K} (\omega + \omega_K) \langle \langle X; Y \rangle \rangle_\omega = - \sum_{K'} \langle \Psi_0 | Y \Psi_{K'} \rangle \langle \Psi_{K'} | X \Psi_0 \rangle = S_{XY}^{K0} \quad (18)$$

where K' runs over all degenerate states corresponding to the excitation energy ω_K . The time-reversal symmetry, Eq. (2), is transferred from the polarization propagator to the line strength S_{XY} through the relation

$$S_{XY}^{0K} = -(S_{XY}^{K0})^*. \quad (19)$$

Moszynski, Żuchowski, and Jeziorski²² have expressed the polarization propagator within the framework of the XCC theory

$$\langle \langle X; Y \rangle \rangle_\omega = \left\langle e^{-S} e^{T^\dagger} Y e^{-T^\dagger} e^S \middle| \hat{\mathcal{P}} \left(e^{S^\dagger} \Omega^X(\omega) e^{-S^\dagger} \right) \right\rangle + \text{g.c.c.}, \quad (20)$$

where g.c.c. (generalized complex conjugate) denotes the complex conjugation of the r.h.s. and substitution of ω for $-\omega$. Not only this expression satisfies the time reversal symmetry, but is also size-consistent because it can solely be represented in terms of commutators.

The operator $\Omega^X(\omega)$ appearing in Eq. (20) is solution of the linear response equation,²²

$$\left\langle \tilde{\mu} \middle| [e^{-T} H e^T, \Omega^X(\omega)] + \omega \Omega^X(\omega) + e^{-T} X e^T \right\rangle = 0, \quad (21)$$

where $\Omega^X(\omega) = \Omega_1^X(\omega) + \Omega_2^X(\omega) + \dots + \Omega_N^X(\omega)$, and $\Omega_n^X(\omega)$ is an excitation operator of the form

$$\Omega_n^X = \sum'_{\mu_n} O_{\mu_n}^X(\omega) \mu_n. \quad (22)$$

where \sum'_{μ_n} stands for restricted summation over non-redundant excitations for double excitations $ai \geq bj$ and for triple excitations $ai \geq bj \geq ck$. Using the transformation from the molecular orbital basis to the Jacobian basis

$$\mu_n = \sum_M \mathcal{L}_{\mu_n M}^* r_M, \quad \tilde{\mu}_n^* = \sum_M \mathcal{R}_{\mu_n M}^* l_M^* \quad (23)$$

$\Omega^X(\omega)$ can be written as

$$\begin{aligned} \Omega^X(\omega) &= \sum_M \sum_{n=1}^N \sum'_{\mu_n} \mathcal{L}_{\mu_n M}^* O_{\mu_n}^X(\omega) r_M \\ &= \sum_M O_M^X(\omega) r_M. \end{aligned} \quad (24)$$

Eq. (21) takes then the form

$$\begin{aligned} \langle l_M | [e^{-T} H e^T, r_M] \rangle O_M^X(\omega) \\ + \omega O_M^X(\omega) + \langle l_M | e^{-T} X e^T \rangle = 0, \end{aligned} \quad (25)$$

where $\langle l_M | [e^{-T} H e^T, r_M] \rangle$ is the M -th excitation energy ω_M , and we used the biorthonormality condition $\langle l_M | r_K \rangle = \delta_{MK}$. The $O_M^X(\omega)$ reads

$$O_M^X(\omega) = - \frac{\langle l_M | e^{-T} X e^T \rangle}{\omega_M + \omega}. \quad (26)$$

We will now translate Eq. (20) into a computationally transparent form. The action of the projection superoperator $\hat{\mathcal{P}} = \hat{\mathcal{P}}_1 + \hat{\mathcal{P}}_2 + \dots + \hat{\mathcal{P}}_N$ on the commutator expansion of $e^{S^\dagger} \Omega^X(\omega) e^{-S^\dagger}$ produces a sum of multiply nested commutators

$$\begin{aligned} \hat{\mathcal{P}} \left(\sum_{n=1}^N \sum'_{\mu_n} \sum_{k=0}^{n-1} \frac{1}{k!} [S^\dagger, O_{\mu_n}^X(\omega)]_k \right) = \\ \sum_{n=1}^N \sum'_{\mu_n} O_{\mu_n}^X \sum_{k=0}^{n-1} \frac{1}{k!} \sum_{\Gamma} [S_{n_1}^\dagger, [\dots [S_{n_{k-1}}^\dagger, [S_{n_k}^\dagger, \mu_n] \dots]], \end{aligned} \quad (27)$$

where the last summation runs over all sequences satisfying the condition

$$\Gamma : k \leq n_1 + \dots + n_k \leq n - 1. \quad (28)$$

Using Eq. (27), the polarization propagator in the molecular orbital basis takes the form

$$\langle\langle X; Y \rangle\rangle_\omega = \sum_{n=1}^N \sum'_{\mu_n} O_{\mu_n}^X(\omega) \gamma_{\mu_n}^Y + \text{g.c.c.}, \quad (29)$$

where we use the shorthand notation for $\gamma_{\mu_n}^Y$ and $\eta(\mu_n)$ respectively

$$\begin{aligned} \gamma_{\mu_n}^Y &= \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \eta(\mu_n) \rangle, \\ \eta(\mu_n) &= \sum_{k=0}^{n-1} \frac{1}{k!} \sum_{\Gamma} [S_{n_1}^\dagger, [\dots [S_{n_{k-1}}^\dagger, [S_{n_k}^\dagger, \mu_n] \dots]]. \end{aligned} \quad (30)$$

Transformation of Eq. (29) to the Jacobian basis leads to the following expression

$$\begin{aligned} \langle\langle X; Y \rangle\rangle_\omega &= \\ &= - \sum_M \frac{\langle l_M | e^{-T} X e^T \rangle \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \eta(r_M) \rangle}{\omega_M + \omega} + \text{g.c.c.}, \\ &= - \sum_M \frac{\xi_M^X \gamma_M^Y}{\omega_M + \omega} + \text{g.c.c.}, \end{aligned} \quad (31)$$

where

$$\begin{aligned} \xi_M^X &= \langle l_M | e^{-T} X e^T \rangle \\ &= \sum_{n=1}^N \sum'_{\mu_n} \mathcal{L}_{\mu_n M} \langle \mu_n | e^{-T} X e^T \rangle \\ &= \sum_{n=1}^N \sum'_{\mu_n} \mathcal{L}_{\mu_n M} \xi_{\mu_n}^X. \\ \gamma_M^Y &= \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \eta(r_M) \rangle \\ &= \sum_{n=1}^N \sum'_{\mu_n} \mathcal{R}_{\mu_n M} \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \eta(\mu_n) \rangle \\ &= \sum_{n=1}^N \sum'_{\mu_n} \mathcal{R}_{\mu_n M} \gamma_{\mu_n}^Y. \end{aligned} \quad (32)$$

The transition strength matrices are computed as the residues of the XCC linear response function

$$S_{XY}^{0K} = - \sum_{K'} \gamma_{K'}^Y \xi_{K'}^X \quad S_{XY}^{K0} = \sum_{K'} (\gamma_{K'}^Y)^* (\xi_{K'}^X)^*. \quad (33)$$

The line strengths are connected by the relation of antihermiticity, Eq. (19), which comes

up naturally in the XCC formalism. As our formulas for the transition strength matrices are exclusively expressed in terms of commutators, they are automatically size intensive, regardless of any truncation of the T or S operators.

We now present the scheme of approximations to the product

$$\gamma_K^Y \xi_K^X = \sum_{n=1}^N \sum'_{\mu_n} \mathcal{R}_{\mu_n M} \gamma_{\mu_n}^Y \sum_{m=1}^N \sum'_{\mu_m} \mathcal{L}_{\mu_m M} \xi_{\mu_m}^X. \quad (34)$$

The explicit expressions for γ_μ^Y and ξ_μ^X in the CC3 approximation are:

$$\begin{aligned} (\gamma_{\mu_1}^Y)^{\text{CC3}} &= \langle (Y + [S_1^\dagger, Y] + [S_2^\dagger, Y] + [S_2^\dagger, [Y, T_1]] \\ &\quad + [S_2^\dagger, [Y, T_2]] + [S_3^\dagger, [Y, T_2]]) \mu_1 \rangle, \\ (\xi_{\mu_1}^X)^{\text{CC3}} &= \langle \mu_1 | X + [X, T_1] + [X, T_2] \rangle, \\ (\gamma_{\mu_2}^Y)^{\text{CC3}} &= \langle ([S_2^\dagger, Y] + [S_3^\dagger, Y] + [S_2^\dagger, [S_1^\dagger, Y]] \\ &\quad + [S_2^\dagger, [Y, T_1]] + [S_3^\dagger, [Y, T_2]]) \mu_2 \rangle \\ &\quad + \langle (Y + [S_2^\dagger, Y]) [S_1^\dagger, \mu_2] \rangle, \\ (\xi_{\mu_2}^X)^{\text{CC3}} &= \langle \mu_2 | [X, T_2] + [X, T_3] \\ &\quad + [[X, T_1], T_2] \rangle, \\ (\gamma_{\mu_3}^Y)^{\text{CC3}} &= \langle ([S_3^\dagger, Y] + [S_2^\dagger, [S_1^\dagger, Y]] \\ &\quad + \frac{1}{2} [S_2^\dagger, [S_2^\dagger, Y]]) \mu_3 \rangle + \langle [S_2^\dagger, Y] [S_1^\dagger, \mu_3] \rangle, \\ &\quad + \langle (Y + [S_1^\dagger, Y] + [S_2^\dagger, Y]) [S_2^\dagger, \mu_3] \rangle, \\ (\xi_{\mu_3}^X)^{\text{CC3}} &= \langle \mu_3 | [X, T_3] + \frac{1}{2} [[X, T_2], T_2] \\ &\quad + [[X, T_1], T_2] \rangle. \end{aligned} \quad (35)$$

The expressions for γ_μ^Y and ξ_μ^X contain contributions up to and including the third order of MBPT. In $\gamma_{\mu_2}^Y$ and $\gamma_{\mu_3}^Y$ we have omitted the third order terms $\frac{1}{2} \langle [S_2^\dagger, [S_2^\dagger, [Y, T_2]]] \mu_2 \rangle$ and $\frac{1}{2} \langle [S_2^\dagger, [S_2^\dagger, [Y, T_2]]] \mu_3 \rangle$ as they are computationally much more demanding than the rest of the contributions. The S_1 and S_2 operators are correct through the third order, and the S_3 operator contains only the leading term correct through the second order, Eq. (13).

All the implementation-ready formulas presented in this work have been derived with the assistance of the **Paldus** program developed in our laboratory. **Paldus** is a program

for an automated implementation of any level of theory expressible through the products of singlet orbital replacement operators. The formulas obtained with **Paldus** program are automatically optimized and incorporated into the parallelized, standalone **Fortran** code.

III. NUMERICAL RESULTS AND DISCUSSION

A. First-order properties at the CC3 level of theory

We present the results for the ground-state dipole moments of diatomic molecules calculated at the XCC3 level of theory. The geometries of the diatomic molecules are kept at their equilibrium values.²⁸ Comparison is done with the experimental data²⁹ and with the LRCC3 results. For all the molecules we employ the def2-QZVPP basis set.³⁰

Figs. 1 to 3 show the unsigned percentage error of the dipole moment relative to the experimental value $\Delta_{\text{rel}} := |\delta q|/|q_{\text{exp}}| \times 100\%$ as a function of the highest-order term included in Eq. (15). In each plot, separate lines represent approximations to the auxiliary operator S , denoted as XCC3S(m). Thus, there are two levels of approximation: one for the expectation value formula, Eq. (15), and one for the operator S , Eq. (14).

In each case, the convergence of the expectation value defined by Eq. (15) is achieved after including the terms up to and including the fifth order. However, the inclusion of the higher-order terms does not introduce much additional computational costs. The most time consuming terms that scale as \mathcal{N}^8 appear in the fourth and higher orders. Introduction of intermediates reduces the scaling of all such terms to \mathcal{N}^7 . As the most expensive terms appear already in the fourth order, computing the full sum, Eq. (15), is essentially of the same cost as computing only the partial sums.

An inspection of Figs. 1 to 3 shows that in all three cases the use of XCC3S(3) brings an improvement over XCC3S(2) relative to the experimental values. The most challenging case is the CO molecule. For this system, the XCC3S(2) level of theory is unacceptable with Δ_{rel} reaching 90%. A huge reduction of this error is observed for XCC3S(3) and XCC3S(4).

Importantly, in every case improving the accuracy of S improves the accuracy of the results. However, going from XCC3S(3) to XCC3S(4) brings only a negligible improvement not worth the corresponding increase in the computational complexity, from \mathcal{N}^7 to \mathcal{N}^8 . We thus recommend the XCCS(3) level of theory; this will be the approximation of S employed

to compute second order properties.

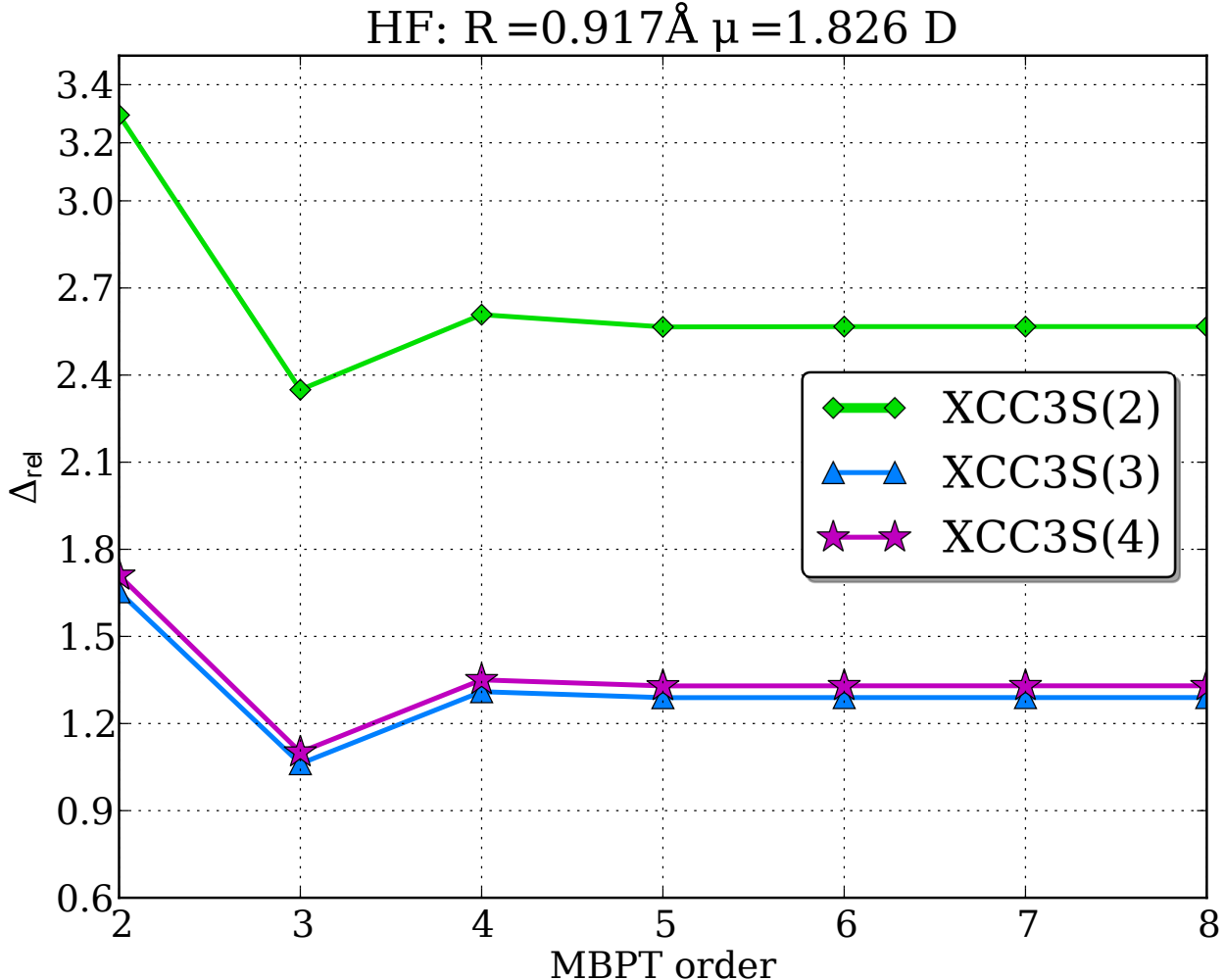


FIG. 1. Δ_{rel} of the dipole moment of HF.

We compare our method with the Lagrangian technique of Hald and Jørgensen.¹³ Table I shows the signed absolute errors of both methods applied to the dipole moments of the test set of diatomics with the experimental data. On the average the XCC3S(3) method is only slightly better than LRCC3. Indeed, the mean absolute error for XCC3S(2) is equal to 0.023 and for LRCC3 is equal to 0.038.

This result is encouraging since the XCC3 method is conceptually simpler and computationally less demanding than the LRCC3 approach. While both methods employ the same model for the ground-state wave function (that scales as $v^4 o^3$, where v and o stand for the number of the virtual and occupied orbitals, respectively), the difference lies in the computation of the auxiliary operators required for the one-electron properties, i.e. the

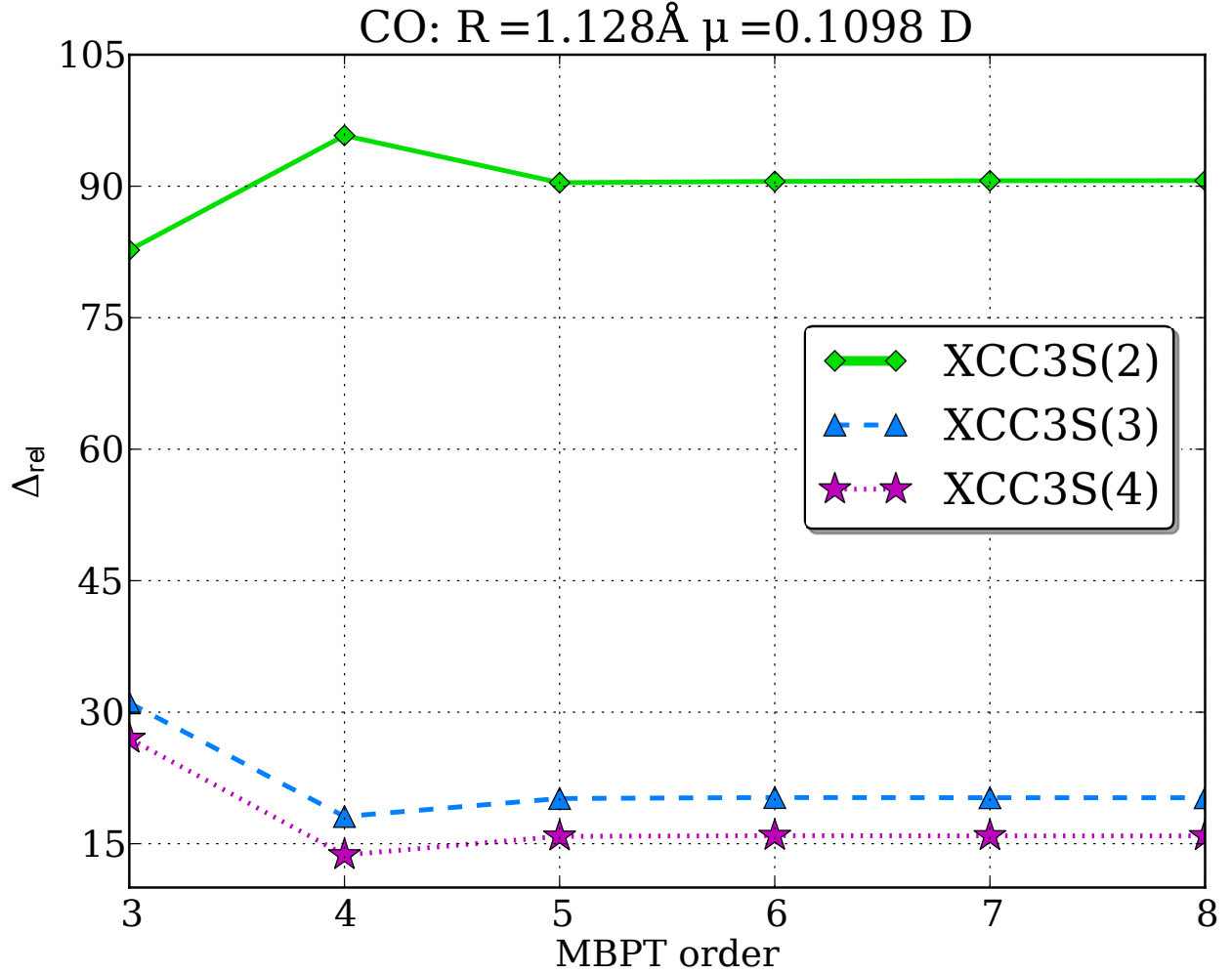


FIG. 2. Δ_{rel} of the dipole moment of CO.

TABLE I. Dipole moments computed with the XCC3S(3) and LRCC3 methods. The def2-QZVPP basis set was employed for molecules at equilibrium geometries. The experimental data are given in Debye, and the computed values are given as a signed error $\Delta_{\text{method}} = \mu_{\text{exp}} - \mu_{\text{method}}$.

molecule	exp.	$\Delta_{\text{XCC3S(3)}}$	Δ_{LRCC3}
LiH	5.884	0.0400	0.0463
HF	1.826	0.0235	0.0071
LiF	6.3274	0.0179	0.0879
CO	0.1098	0.0222	-0.0264
NaLi	0.463	-0.0107	-0.0263
HCl	1.1086	0.0169	-0.0216
NaF	8.156	-0.0015	0.0812
CS	1.958	0.0530	0.0055

Lagrangian multipliers in the case of the LRCC approach and the operator S in the case

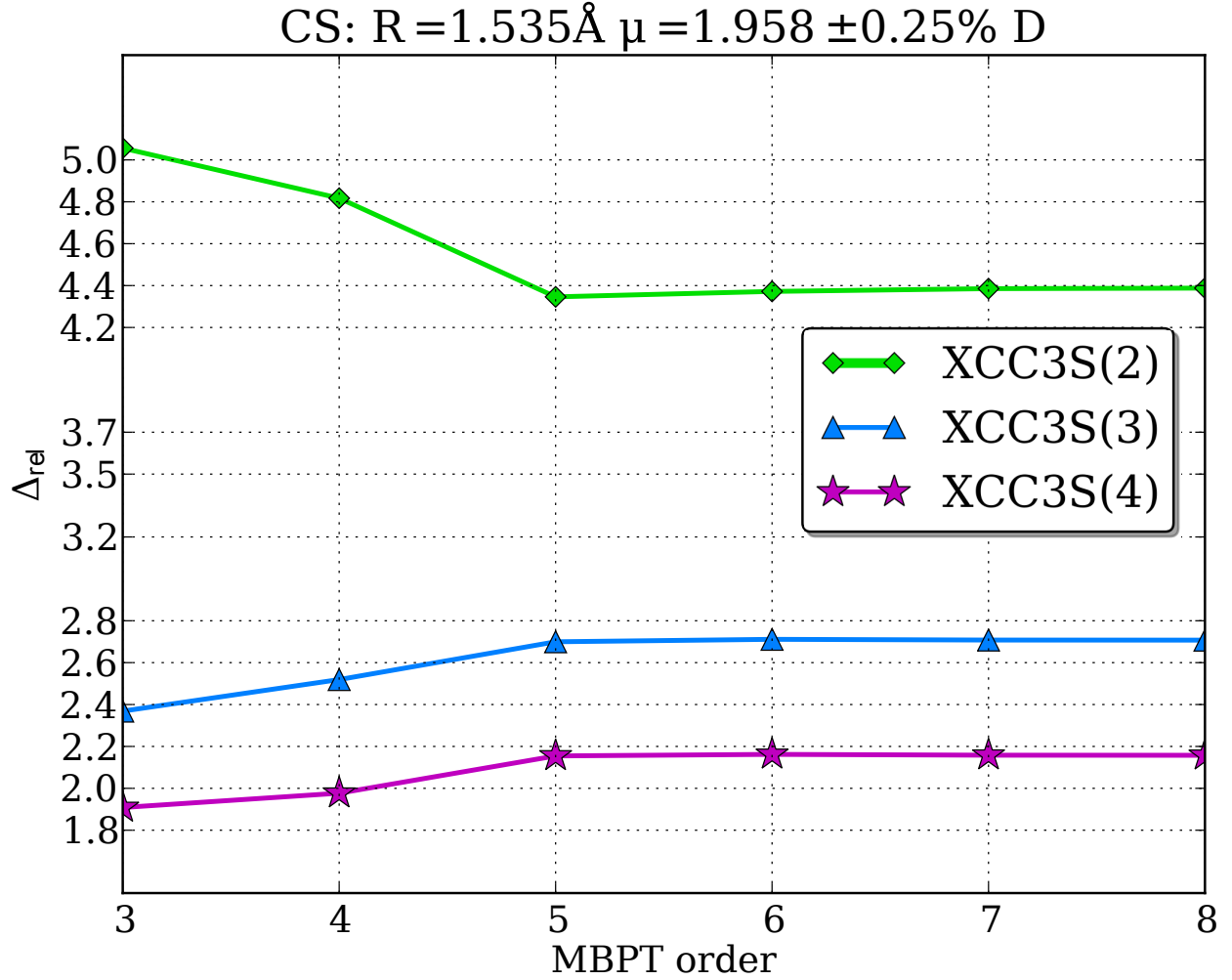


FIG. 3. Δ_{rel} of the dipole moment of CS.

of the XCC method. The equations for the singles and doubles Lagrangian multipliers are solved iteratively and each iteration scales like $v^4 o^2$, whereas the amplitudes of the S_1 and S_2 operators are computed directly in a single step that scales as $v^3 o^3$. Moreover, S_3 can efficiently be approximated by T_3 , whereas the most expensive, triples Lagrange multipliers in the LRCC3 approach have to be computed separately. The computational complexity of assembling the density matrices from the auxiliary amplitudes, ground-state amplitudes, and molecular integrals is the same in both approaches and scales as $v^4 o^3$.

B. Transition probabilities

We have performed computations of the electric dipole transition probabilities between the ^1S and ^1P states for the Mg, Ca, Sr and Ba atoms, and of the quadrupole transition

probabilities between the ^1S and ^1D states for the Ca and Ba atoms.

The line strength of the dipole transition is defined as

$$S_d = \sum_{K,K'} |\langle K | \mathbf{d} | K' \rangle|^2 \quad (36)$$

where K and K' run over all degenerate states, and \mathbf{d} is the dipole moment operator. The dipole transition probability $A_{1\text{P}^1\text{S}}$ is related to the line strength by the relation³¹

$$A_{1\text{P}^1\text{S}} = \frac{1}{3} \frac{16\pi^3}{3h\epsilon_0\lambda^3} S_d^{1\text{P}^1\text{S}}, \quad (37)$$

where SI units are used for $A_{1\text{P}^1\text{S}}$, S_d and λ : s^{-1} , $\text{m}^2 \text{C}^2$ and m respectively.

The strength of a quadrupole transition is defined as³²

$$S_q = \sum_{K,K'} |\langle K | \mathbf{Q} | K' \rangle|^2, \quad (38)$$

where \mathbf{Q} is the traceless quadrupole moment operator in the Shortley's convention,³² and the transition probability reads

$$A_{1\text{D}^1\text{S}} = \frac{1}{5} \frac{32\pi^6}{5h\lambda^5} S_q^{1\text{D}^1\text{S}}, \quad (39)$$

where SI units are used for $A_{1\text{D}^1\text{S}}$, S_q and λ : s^{-1} , $\text{m}^4 \text{C}^2$ and m respectively. A_{ki} will be used as a shorthand notation for both dipole and quadrupole transition probabilities.

1. *Dipole transition probabilities*

Table II shows the atomic transition probabilities A_{ki} for the $^1\text{S} - ^1\text{P}$ transitions in Mg, Ca, Sr, and Ba atoms. The results are compared with the available spectroscopic data. In each case we performed calculations with the XCC3S(2), XCC3S(3), and LRCC3 methods. To illustrate the convergence of the computed dipole transition probabilities with the basis set size, we use a progression of basis sets.

We also performed computations with the multireference configuration interaction (MRCI) method restricted to single and double excitations in order to compare our method with approaches based on different models of the wave function. Numerical results for the dipole

transition probabilities are presented in the last two columns of Table II. The MRCI results were obtained with the Molpro program.³³ In all cases, except for the Ba atom, the agreement with the experiment of the MRCI data is by an order of magnitude worse than of the results obtained with the XCC and LRCC methods.

Except for the Ba case, the results converge quickly to the experimental benchmarks with the increase of the basis set size. In all other cases, for the largest bases employed, the results are well within the experimental error bars. For the Ba atom no improvement of the XCC, LRCC, or the MRCI values is observed with the enlargement of the basis. This can probably be attributed to the use of the pseudopotential that treats the core-electron correlation in an approximate way. In the case of Mg, Ca, and Sr atoms the use of XCC3S(3) shows a significant improvement over XCC3S(2). This corroborates the choice of XCC3S(3) as the recommended approach. The comparison of XCC3S(3) with LRCC3 shows that the transition probabilities are of the same quality.

Although the transition probabilities obtained with the XCC3 and LRCC3 methods are of equivalent quality, the computational steps required to obtain these properties differ, with XCC3 being the simplest approach. From the computational point of view, the major additional cost of LRCC3 is the calculation of the matrix $F_{\mu\nu}^X = \langle \Lambda[[X, \mu]\nu]|\Psi \rangle$ and obtaining the \mathbf{F} -transformed vectors.^{19,21,34} Moreover, the LRCC3 approach involves (as in the case of ground-state properties) an iterative computation of the Lagrange multipliers, while the XCC3 method requires only a single step calculation of the S amplitudes. The remaining steps, i.e. the diagonalization of the Jacobian matrix and solution of the response equation Eq. (21), are the same for both methods.

2. *Quadrupole transition probabilities*

Electric quadrupole transitions are difficult to observe due to the very long lifetimes of the atomic D states. For closed-shell atoms only the calcium and barium atomic 1D states are directly connected with the ground 1S states through the E2 transition. For the calcium atom two measurements of the quadrupole transition probabilities were reported^{42,43} with error bars that exclude one the other. Thus, accurate theoretical determination can discriminate between the two measurements. For barium the (old) experimental result⁴⁴ with relatively large error bars does not agree with any theoretical determination.^{45–47} Thus, the present

TABLE II. Dipole transition probabilities obtained with the XCC3, LRCC3, and MRCI methods. All A_{ki} values given in $10^8 s^{-1}$. $\Delta = A_{ki}^{\text{exp}} - A_{ki}^{\text{comp}}$. T = def2-TZVP³⁰, Q = def2-QZVP³⁰, 5 = cc-pV5Z^{35,36}, E46 = ECP46MDF³⁷.

Mg $3s^2 - 3s3p$: $A_{ki}^{\text{exp}} = 4.95(15)^{29,38}$								
	$A_{ki}^{S(2)}$	$\Delta^{S(2)}$	$A_{ki}^{S(3)}$	$\Delta^{S(3)}$	A_{ki}^{LR}	Δ^{LR}	A_{ki}^{MR}	Δ^{MR}
T	5.808	-0.858	5.876	-0.926	5.882	-0.932	6.04	1.09
Q	4.777	0.173	4.833	0.117	4.843	0.107	4.80	-0.15
5	4.796	0.154	4.853	0.097	4.864	0.086	4.83	-0.12
Ca $4s^2 - 4s4p$: $A_{ki}^{\text{exp}} = 2.20(4)^{38,39}$								
	$A_{ki}^{S(2)}$	$\Delta^{S(2)}$	$A_{ki}^{S(3)}$	$\Delta^{S(3)}$	A_{ki}^{LR}	Δ^{LR}	A_{ki}^{MR}	Δ^{MR}
T	2.352	-0.152	2.385	-0.185	2.386	-0.186	2.71	0.51
Q	2.183	0.017	2.211	-0.011	2.212	-0.012	2.64	0.44
5	2.159	0.041	2.184	0.016	2.184	0.016	2.62	0.42
Sr $5s^2 - 5s5p$: $A_{ki}^{\text{exp}} = 2.01(3)^{38,40}$								
	$A_{ki}^{S(2)}$	$\Delta^{S(2)}$	$A_{ki}^{S(3)}$	$\Delta^{S(3)}$	A_{ki}^{LR}	Δ^{LR}	A_{ki}^{MR}	Δ^{MR}
T	2.067	-0.057	2.089	-0.079	2.089	-0.079	2.17	0.16
Q	1.971	0.039	1.994	0.016	1.993	0.017	2.39	0.38
Ba $6s^2 - 6s6p$: $A_{ki}^{\text{exp}} = 1.19(4)^{38,41}$								
	$A_{ki}^{S(2)}$	$\Delta^{S(2)}$	$A_{ki}^{S(3)}$	$\Delta^{S(3)}$	A_{ki}^{LR}	Δ^{LR}	A_{ki}^{MR}	Δ^{MR}
T	1.285	-0.095	1.295	-0.105	1.290	-0.100	1.65	0.46
Q	1.312	-0.122	1.324	-0.134	1.323	-0.133	1.81	0.62
E46	1.305	-0.115	1.319	-0.129	1.312	-0.122	1.87	0.68

results will shed some light on the accuracy of the measurements and calculations.

For Ca, we computed the $4s^2 - 3s^1 4s^1$ quadrupole transition probability with the XCC3S(3) method in the def2-QZVPP basis set.³⁰ The experimentally measured energy is 21849.63 cm^{-1} .⁴⁸ As the energy in Eqs. (37) and (39) is present in third and fifth power, respectively, small error in the computed energy introduces a large error in the transition probability. Therefore, we present the transition probabilities computed with both theoretical and experimental energy input.

TABLE III. Quadrupole transition probabilities for Ca. The XCC3 and LRCC3 computations were performed in the cc-pV5Z basis set.^{35,36}

$A \text{ s}^{-1}$	$S \text{ E year}$	Ref.
87	T T 1980	Ref. 49
40 ± 8	E E 1982	Ref. 42
81	T T 1981	Ref. 50
39.6	T T 1985	Ref. 51
60.2	T T 1983	Ref. 52
70.5	T T 1991	Ref. 53
54.4 ± 4	E E 2003	Ref. 43
49.42	T T 2008	Ref. 54
66.44	T T 2014	MRCI
58.56	T E 2014	MRCI
56.08	T T 2014	LRCC3
51.11	T E 2014	LRCC3
56.05	T T 2014	XCC3S(3)
51.08	T E 2014	XCC3S(3)

Table III shows the result for the calcium E2 transition that have been published to date. In the second and third columns, T stands for theoretically and E for experimentally obtained value for the line strength and energy, respectively. The present theoretical results are well within the error bars of the 2003 measurement⁴³ and outside the error bars of the older 1982 measurement.⁴² Note that the XCC3 and LRCC3 results are very close to each other despite quite different theoretical approaches that are on the basis of these methods. Thus, we can conclude that the present study supports the experimental result from 2003.⁴³

We also computed the quadrupole transition probabilities for the calcium atom with the MRCI method as this approach is based on a different model of the wave function. The results obtained with both the theoretical and experimental excitation energies are outside the error bars of the experiment from 2003. However, the value of the quadrupole transition probability calculated with the experimental excitation energy differs only by 1% from the experimental result of Beverini *et al.*⁴³ which confirms once more that the experimental result from 2003 is more probable.

There are only a few theoretical values^{45–47} for the $6s^2 - 6s5d$ transition in Ba, and only one experimental result.⁴⁴ The experimental transition energy is equal to 11395.35 cm^{-1} .⁴⁸ We have employed the ECP46MDF pseudopotential and the corresponding *spdfg* basis.^{37,55}

Table IV compiles the published results for the $6s^2 - 6s5d$ Ba quadrupole transition. None of the earlier theoretical results as well as the present XCC3 and LRCC3 results, are within the experimental error. One should notice though that the experimental value error bars show a huge uncertainty. The MRCI transition probabilities, both with the theoretical and experimental excitation energies, are also far from the experimental value. Note also that for the Ba atom the MRCI results are significantly different from both the LRCC3 and XCC3 results.

TABLE IV. Quadrupole transition probabilities for barium.

A s^{-1}	S	E	year	Ref.
3.2	T	T	1974	Ref. 45
2.98	T	T	1984	Ref. 46
3.381	T	T	1990	Ref. 47
3.880	T	E	1990	Ref. 47
8 ± 3	E	E	1981	Ref. 44
2.47	T	T	2014	MRCI
1.42	T	E	2014	MRCI
3.49	T	T	2014	LRCC3
2.85	T	E	2014	LRCC3
3.52	T	T	2014	XCC3S(3)
2.87	T	E	2014	XCC3S(3)

IV. CONCLUSIONS

We have presented an extension of the coupled cluster method designed for the computation of the ground state properties and transition probabilities. In order to test the performance of our method, we have computed dipole moments for several diatomic molecules. The results were compared to the experimental data. A comprehensive analysis showed that the best compromise between accuracy and computational cost is achieved for the XCC3S(3) variant, i.e. for the third-order approximation to the auxiliary operator.

We have reported the expressions for the transition density matrices computed from the Hermitian formulation of the polarization propagator in the XCC3 approximation. In contrast to the LRCC3 method, the correct time-reversal symmetry of the line strength is

guaranteed by the algebraic construction of the polarization propagator in the XCC theory and its approximate variants.

The results of the transition probabilities computed with both the XCC3 and LRCC3 methods are of the same quality, though XCC is computationally less demanding. The same conclusion holds for the XCC3 and LRCC3 dipole moments.

The computed dipole and quadrupole transition probabilities were compared with the experimental data, and in most cases the results were in a perfect agreement with the experiment. Our results for the quadrupole transition probabilities in the calcium atom with both the XCC3 and LRCC3 methods strongly favor the new measurement of 2003.⁴³ Our results for the Ba atom are consistent with all the other theoretical data, suggesting that the experimental determination should be reconsidered.

The code for transition moments from the ground state will be incorporated in the KOŁOS: A general purpose ab initio program for the electronic structure calculation with Slater orbitals, Slater geminals, and Kołos-Wolniewicz functions.

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Appendix: Biorthonormal, nonredundant basis for the triply excited manifold

The general bra and ket vectors in the triply excited manifold are denoted as $\langle_{i_1 i_2 i_3}^{a_1 a_2 a_3}|$ and $|_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle$, where the sequence of virtual-occupied electron pair indices is decreasing from left to right. In the case where all indices are different ($a_1 > a_2 > a_3$ and $i_1 > i_2 > i_3$) the

biorthonormal set is defined as :

$$\begin{aligned}
v_1 &= |a_1 a_2 a_3\rangle_{i_1 i_3 i_2}, & v_2 &= |a_1 a_2 a_3\rangle_{i_2 i_1 i_3}, & v_3 &= |a_1 a_2 a_3\rangle_{i_2 i_3 i_1}, \\
v_4 &= |a_1 a_2 a_3\rangle_{i_3 i_1 i_2}, & v_5 &= |a_1 a_2 a_3\rangle_{i_3 i_2 i_1}, \\
\tilde{v}_1 &= \frac{\langle a_1 a_2 a_3 |}{4} + \frac{\langle a_1 a_2 a_3 |}{12} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{12}, \\
\tilde{v}_2 &= \frac{\langle a_1 a_2 a_3 |}{12} + \frac{\langle a_1 a_2 a_3 |}{4} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{12}, \\
\tilde{v}_3 &= \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{3} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6}, \\
\tilde{v}_4 &= \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{3} + \frac{\langle a_1 a_2 a_3 |}{6}, \\
\tilde{v}_5 &= \frac{\langle a_1 a_2 a_3 |}{12} + \frac{\langle a_1 a_2 a_3 |}{12} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{6} + \frac{\langle a_1 a_2 a_3 |}{4}.
\end{aligned} \tag{A.1}$$

The vectors in Eq. (A.1) satisfy $\langle \tilde{v}_k | v_l \rangle = \delta_{kl}$. Note that in this case there are only five linearly independent bra/ket vectors. If some of the indices are equal, there are three cases to consider:

1. A single equality among the occupied indices (either $i_1 = i_3$ or $i_2 = i_3$)

$$\langle \widetilde{a_1 a_2 a_3} |_{i_1 i_2 i_3} = \frac{1}{3} \langle a_1 a_2 a_3 |_{i_1 i_2 i_3} + \frac{1}{6} \langle a_1 a_2 a_3 |_{i_2 i_1 i_3} \tag{A.2}$$

2. A single equality among the virtual indices (and an additional constraint on the occupied indices: $\neg(i_1 > i_2 > i_3)$)

$$\langle \widetilde{a_1 a_2 a_3} |_{i_1 i_2 i_3} = \frac{1}{3} \langle a_1 a_2 a_3 |_{i_1 i_2 i_3} + \frac{1}{6} \langle a_1 a_2 a_3 |_{i_3 i_2 i_1}. \tag{A.3}$$

3. A single equality among the occupied indices and among the virtual ones (the equalities are indicated by repeating labels; additionally, the strict inequalities $a_1 > a_2$ and $i_1 > i_2$ hold)

$$\begin{aligned}
\langle \widetilde{a_1 a_1 a_2} |_{i_1 i_2 i_1} &= \frac{1}{2} \langle a_1 a_1 a_2 |_{i_1 i_2 i_1}, & \langle \widetilde{a_1 a_1 a_2} |_{i_1 i_2 i_2} &= \frac{1}{2} \langle a_1 a_1 a_2 |_{i_1 i_2 i_2}, \\
\langle \widetilde{a_1 a_2 a_2} |_{i_2 i_1 i_2} &= \frac{1}{2} \langle a_1 a_2 a_2 |_{i_2 i_1 i_2}, & \langle \widetilde{a_1 a_2 a_2} |_{i_1 i_1 i_2} &= \frac{1}{2} \langle a_1 a_2 a_2 |_{i_1 i_1 i_2}.
\end{aligned} \tag{A.4}$$

All vectors that do not fit into the above defined templates are deemed linearly dependent

and discarded from the basis. Note that this is one of possible choices of the biorthonormal nonredundant basis.

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